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Metal effect pigments for reducing flow line visibility

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Abstract

Metallic appearance of injection moulded polymer parts is favoured in many industries, e.g. packaging or automotive. Filling polymers with metal effect pigments avoids additional coating steps, however, visible inhomogeneities in the metallic appearance suggest low part quality. Metallic appearance is generated due to the orientation of planar pigment particles in the flow direction, usually parallel to the part surface. Nevertheless, where polymer fronts merge, this orientation is disturbed, resulting in light scattering and creating dark streaks called flow lines. This paper aims at reporting novel tetrahedron shaped metal effect pigment particles for reducing flow lines, as well as novel particle manufacturing methods.

Two manufacturing methods for tetrahedral particles were examined. In the first method, a file tool is used featuring a cutting surface consisting of pyramidal cutting edges with tetrahedral interstices in between. The file is linearly moved across the surface of bulk Al99.5 under normal force. The aluminium fills the tetrahedral interstices, forming tetrahedral particles, which are then removed. In the second manufacturing method, molten tin is poured onto an aluminium coated silicone rubber patch featuring tetrahedral recesses, and covered by a polyimide lid. After cooling, the particles are removed using a brush.

In flow tests, a compound featuring tetrahedral particles (edge length 75-90 µm) in a silicone fluid matrix (viscosity 97 N·s·m⁻²) was compared to a second compound featuring conventional planar particles (diameter 100 µm) in the same matrix. Both compounds were injected into transparent moulds, letting polymer flow fronts merge and granting in-process observation of the flow line visibility during flow. Particle orientation in the flow line region was examined in a 3D x-ray tomoscopy (time-resolved tomography).

The examined tetrahedral particles did not create the characteristic flow lines of conventional planar pigment particles. By the described manufacturing methods, the manufacturability of tetrahedral metal particles was proved in the range of grams.

Keywords: composite, flow, injection, moulding

1. Introduction

The requirement of metallic appearance of polymer parts exists in various applications, where a metallic look signals high value. The use of metal effect pigments as filler is a key technology to achieve metallic appearance on polymer parts while avoiding additional coating steps. Thus, polymer matrix composites with a disperse phase of metal particles are used in automotive, packaging, consumer electronics, cosmetics, and other industries.

Injection moulding or extrusion are predestined manufacturing processes for mass production of polymer parts. In part manufacturing, metal effect pigments are generally added to the polymer melt via highly filled additive dispersions [1] to achieve the desired volume fraction in the part, typically in the one-digit vol.-% region. Conventional metal effect pigments exhibit planar geometry in order to allow pigment orientation in the polymer melt parallel to the melt flow direction. This results in their main function: Many adjacent particles reflect the light, allowing either a sparkling or shiny appearance of the solidified polymer part without the need of additional coating.

A problem, which has not yet been solved, is the elimination of dark streaks called flow lines (Fig. 1 a). Those are discussed to be either caused by local de-orientation or de-mixing of particles.

According to Wissling et. al., the formation of flow lines is caused by the geometric anisotropy of metal effect pigment particles. Due to the laminar melt flow, the parallel particle orientation is disturbed at the melt front (Fig. 1 b) [2]. In melt front merging regions called weld lines, the disturbed orientation persists during polymer solidification. Schoppe and Ringan further hypothesize a pigment concentration deficit in the flow line region [3].

Flow lines occur wherever the local melt flow direction differs from the global flow direction. Those regions are weld lines, near gates or where the part thickness differs abruptly, being the reason of flowlines at surfaces opposing reinforcement ribs.

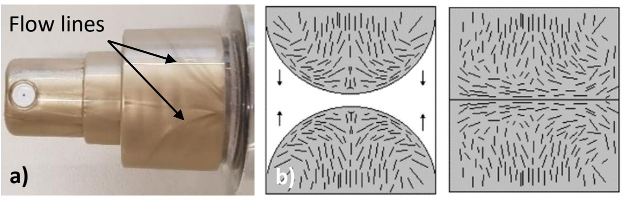


Figure 1. a) Flow lines on a ring- shaped polymer part filled with metal effect pigments of planar particle geometry. b) Scheme of the pigment orientation in weld lines (adapted from [2])

To eliminate flow lines, part designers are constrained, and often, sophisticated flow simulations are required to shift flow lines into non-visible areas. This is costly and time-consuming. Approaches to eliminate flow lines have been pursued. Shear controlled orientation in injection moulding (SCORIM) blurs flow lines by using two pistons, which keep the melt in motion until complete solidification [2,4]. However, this system requires two runners and gates, which ultimately leads to an often undesired weld line. Moreover, the machine has to be equipped with the SCORIM system while the mould requires adaptation.

Conventional manufacturing of metal effect pigments is based on cold forming of atomized metal powder, using a ball mill and separating agent to prevent cold welding [5]. This process requires several sophisticated sieving steps in order to achieve a narrow size distribution and high particle geometry fidelity. Moreover, conventional metal effect pigment manufacturing is limited to manufacture planar pigment particles. Despite geometric anisotropy of the particles being the cause for flow lines, planar faces are required for light reflection. Thus, it is hypothesized that tetrahedral pigment particles do not show flow lines due to their geometric isotropy, while their faces reflect the light regardless. However, neither tetrahedral pigment particles nor their manufacturing is documented.

The study described in this paper aims at the examination of metal effect pigments featuring novel tetrahedral particle geometry to eliminate flow lines without the need of additional moulding systems such as the SCORIM system. In a second aspect, the feasibility of manufacturing methods for tetrahedral metal particles of adaptable size is investigated.

2. Methodology

The object of the study described in this paper is a novel metal effect pigment with tetrahedral geometry, as well as its manufacturing. The feasibility of two manufacturing methods has been investigated: pigment shaping using a specialized file tool, and pigment casting. Subsequently, the flow line formation during injection into a mould was optically investigated. Additionally, the orientation of the particles in a weld line during flow was investigated in-situ using x-ray tomoscopy [6].

2.1. Pigment manufacturing by shaping

The feasibility of shaping tetrahedral metal micro particles was investigated using a file tool consisting of a brass substrate with an edge length of 10x10x8 mm coated with a 2 mm thick layer of NiP featuring adjacent pyramidal protrusions with a height of 33 µm (Fig. 2). Those protrusions were machined on a modified ultra-precision machining centre MMC 1100, LT-ULTRA, GERMANY, using a diamond tool.

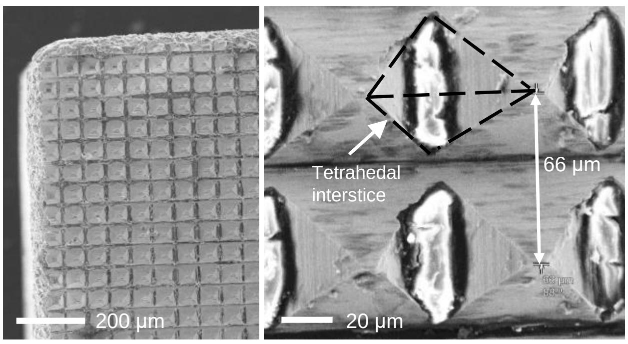


Figure 2. SEM image of the pigment shaping tool

To manufacture tetrahedral pigment particles, the referred tool was linearly moved across the surface of bulk aluminium (99.5% Al) under normal force of 10 kN (Fig. 3). This plastically deformed the aluminium to fill the tetrahedral interstices between the pyramidal protrusions of the tool. Two faces of the thus produced tetrahedral aluminium particles were formed by the contact to the pyramidal tool protrusions, while the other two faces were formed due to shear and subsequent friction between particle and remaining bulk material.

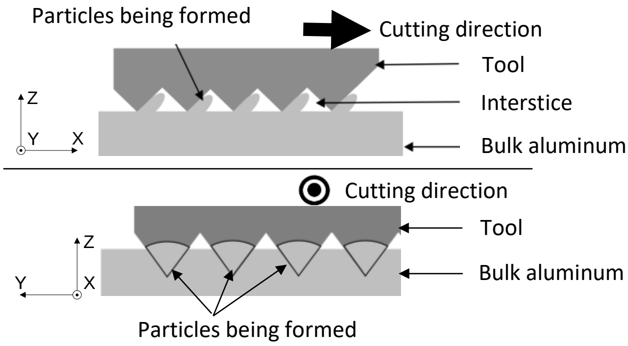


Figure 3. Forming of particles. ***Top:*** Side view, ***Bottom:*** front view

To remove the pigment particles from the tool, brushing and removal by adhesive film were tested while liquid Polydimethylsiloxane (PDMS) AK 100, WACKER, GERMANY, with a viscosity of 97 $N\cdot s\cdot m^{-2}$ at 25 °C was applied to the tool as release agent. Subsequent to their removal, the particles were examined using scanning electron microscopy (SEM).

2.2. Pigment manufacturing by casting

The feasibility of casting tetrahedral micro particles was investigated using a silicone rubber mould featuring tetrahedral cavities with a depth of 100 µm. The mould was replicated as a negative from a brass master structure machined using a diamond tool on an ultra-precision machining centre MMC 1100. The silicone used for the mould was SILASTIC™ RTV-4250, DOW, USA. The silicone mould was coated with aluminium by evaporation deposition in order to increase the wettability by molten Sn99Cu1 used for casting tetrahedral particles.

The melt was cast onto the preheated mould at 250 °C and covered with a polyimide (PI) lid under pressure of 3 N/cm^2. Subsequent to solidification, the pigment particles were removed using a brush.

2.3. Optical flowline investigation during injection

In order to evaluate the formation of flow lines in situ, the cast and sieved tetrahedral particles were dispersed into PDMS fluid AK 100 000, WACKER, GERMANY, which has a viscosity of 97 $N\cdot s\cdot m^{-2}$ at 25 °C. The particle volume fraction was 0.3 %.

For comparison, a second compound was prepared, consisting of the same type of silicone fluid with a disperse phase of conventional metal effect pigments REFLEXAL 100, ECKART, GERMANY, with 100 µm diameter.

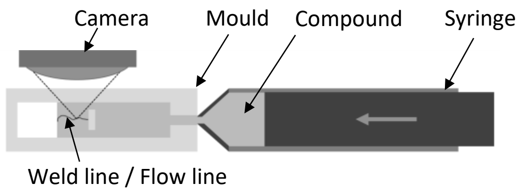


Figure 4. Test setup for optical flowline investigation during injection

The referred compounds were injected into a transparent mould at room temperature with a flow rate of 70 to 80 mm^3/s using a medical syringe with 10 mm piston diameter (Fig. 4). The mould features a symmetrical film gate and a cylindrical obstacle of 6.5 mm diameter, which is positioned 8 mm behind the gate in order to cause two converging flow fronts. The cavity has a cuboid shape with a size of 50x30x1 mm, whereas the two largest faces are made of glass and the remaining structure of 6061 aluminium alloy.

To investigate flowline formation during flow, the injection process was recorded using a digital camera. Replacing a thermoplastic melt with fluid PDMS in this investigation allowed the examination of the same compound multiple times without thermal degradation.

2.4. X-ray tomoscopy during flow

The optical investigation described above was limited to 2D images and conducted with particle volume fractions of 0.3 %, however, volume fractions in the one-digit range reflect industrial applications better. Thus, absorption-based and phase contrast x-ray tomoscopy of the particles was conducted during flow. The flowline formation and particle orientation was examined in 3D at particle volume fractions of 1 %. For those investigations, the TOMCAT-BEAMLINE at PAUL SCHERRER INSTITUTE, SWITZERLAND, equipped with the GIGAFROST camera system, was used. In this setup, a voxel size of 2.75 µm was achieved.

The experimental setup for the tomoscopic investigation was as follows: A PI tube with an inner diameter of 4.06 mm and 70 µm wall thickness was prepared with a cylindrical obstacle of 1.5 mm diameter (Fig. 8 a) and placed in the optical path of the beamline, onto a support rotating at a speed of 300 min^{-1}. The compound was filled into the tube and investigated during gravity driven flow for 100 s, in which 500 tomograms were taken. To prevent air being trapped in the tube below the compound, the PI tube featured exhaust bores near the bottom.

3. Experimental results

3.1. Results of pigment manufacturing by shaping

The shaped particles (Fig. 5) show tetrahedral geometry given by the tool interstices, in which the particles were formed (Fig. 2). The particle edge lengths were 50 to 60 µm, as randomly measured using SEM, differing slightly from the 66 µm distance between the pyramid tips on the tool. Shallow grooves on the pyramidal tool protrusions, having a width in the lower one-digit micrometre range, were replicated to the particle surfaces, indicating potentially high replication accuracy.

However, other regions on the particle surfaces are rugged, implying insufficient filling of tool interstices with aluminium. Small burrs can be seen protruding from the edges of the particles opposite to the cutting direction. Because different particles show the burrs at the same edge, respectively, the burrs are assumed to indicate misalignment of the tool and the cutting direction resulting in aluminium rests not completely being sheared off from the particles.

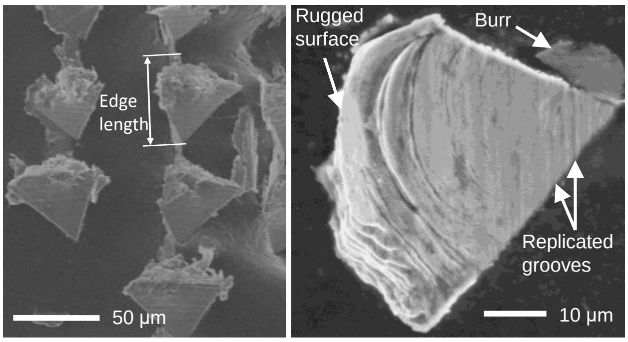


Figure 5. SEM image of tetrahedral particles manufactured by shaping

With the aid of PDMS fluid AK 100 as a release agent being deployed to the tool before shaping, removal of particles was possible using a brush, provided that the bristle tips fit into the interstices. For example, human hair with a diameter of about 20-30 µm proved capable of sufficiently removing the particles from the tool without damaging the particles.

Removal by adhesive tape proved to remove most of the particles, but required prior cleansing with isopropanol due to a layer of release agent remaining on the particle surfaces after the shaping process, preventing adhesion of the tape.

Alongside the geometrically defined particles, geometrically undefined aluminium grit was produced, however, most of which did not adhere strongly to the tool. Thus, cleansing of the tool without washing away the particles was possible by flushing the tool with isopropanol. Most of the particles removed from the tool by brushing or adhesive tape had tetrahedral shape, indicating the potential of the shaping method to produce particles of narrow size distribution with reduced sieving effort.

3.2. Results of pigment manufacturing by casting

Coating the silicone rubber mould with aluminium was crucial for the particle geometry fidelity. The coating deposited by evaporation deposition did not sufficiently adhere to the silicone mould surface and had to be renewed after every two particle replication cycles.

Compared to the shaped particles (Fig. 5), the cast particles show round edges, presumably caused by the high surface tension of the metal melt (Fig. 6). Unlike the shaping method, casting produced more grit and a large size distribution of tetrahedral particles. The cause was identified to be insufficient filling of several cavities due to low wettability of the mould by the metal melt. This made sieving of the particles necessary, resulting in particle sizes from 35 to 120 µm edge length per cast. Particle removal from the silicone rubber mould was effortlessly possible using a brush, without the need of any release agent.

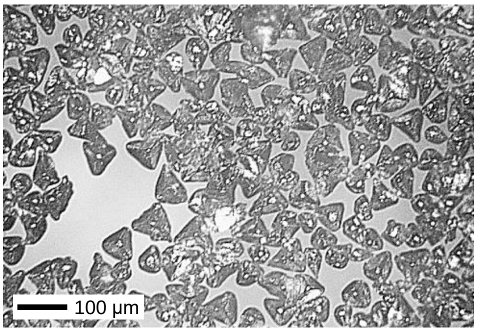


Figure 6. Light microscope image of cast and sieved tetrahedral particles (sieve mesh size 75-90 µm, one sieving step)

3.3. Macroscopical flowline investigation

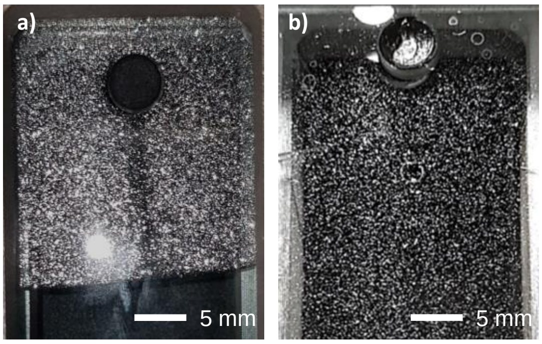


Figure 7. Optical investigation of compounds during injection into a transparent mould. *a)* Conventional metal effect pigments showing a flow line. *b)* Tetrahedral metal effect pigments showing no flow line

As shown in Fig. 7, the compound containing tetrahedral particles did not form a flow line when converging behind the cylindrical obstacle. The compound containing conventional particles however, shows a clearly visible flow line.

3.4. Investigation of the particle behaviour

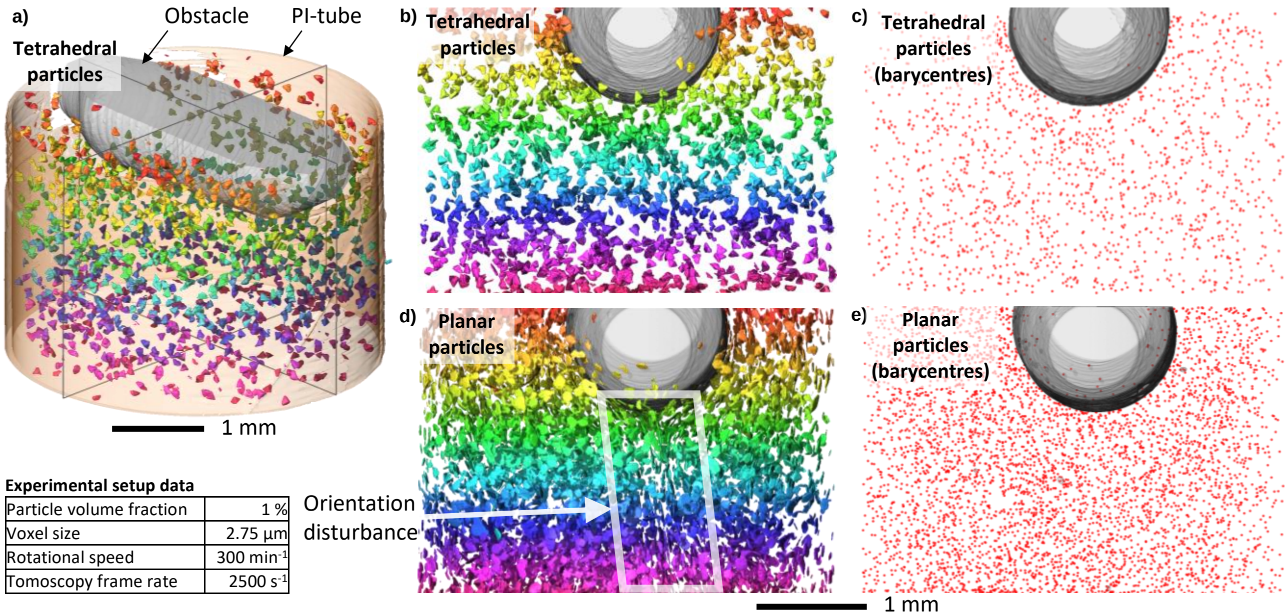
As shown in Fig. 8 b, the compound containing tetrahedral particles shows random particle orientation in the weld line and surrounding areas. In contrast, the conventional platelet shaped particles exhibit an orientation disturbance, where the flow fronts merged after having passed around the obstacle (Fig. 8 d). This distinctive particle orientation in the weld line was observed through the whole compound thickness at any time after the flow fronts merged. As shown in Fig. 8 c and e, the particles did not exhibit any de-mixing in the weld line region, regardless of their geometry. Centrifugal separation due to probe rotation was not observed qualitatively.

barycentres of tetrahedral and platelet shaped particles, de-mixing in the weld line was not visible. This, in contrast to the pigment concentration deficit in the flow line region hypothesized by Schoppe and Ringan, indicates the main reason for the flow line being the geometric anisotropy of particles.

Thus, it can be assumed that the degree of flow line visibility can be controlled by the degree of geometric anisotropy of the pigment particles.

Future research will be conducted towards further evaluation of the 3D x-ray tomography regarding particle trajectories, as well as rheological examination of the novel compound.

The manufacturing method will be optimized in terms of tool interstice filling to improve the particle geometry fidelity. Moreover, other mould materials will be investigated to replace silicone rubber in order to cast particles made of aluminium and other metals. Another aspect will be increasing the output of the



Particle volume fraction	1 %
Voxel size	2.75 µm
Rotational speed	300 min^{-1}
Tomoscopy frame rate	2500 s^{-1}

Figure 8. 3D x-ray tomoscopy images of tetrahedral particles dispersed in silicone fluid flowing around a cylindrical obstacle in a tube. One timeframe at the end of the flow test is displayed. False colours indicate horizontal particle position. *a)* Isometric view on the probe containing tetrahedral particles. *b)* Front view on the probe containing tetrahedral particles. *c)* Barycentres of the tetrahedral particles in image *b*. *d)* Front view on the probe containing conventional planar metal effect pigments. *e)* Barycentres of the planar metal effect pigment particles in image *d*.

4 Conclusions

In this paper, a novel metal effect pigment being able to eliminate flow lines in injection moulded polymer parts was introduced. The feasibility to manufacture the pigment by either shaping or casting was proven. Compared to conventional manufacturing of metal effect pigments by atomization of metal and subsequent cold forming, the particle shaping method is not in need of metal melting, and the casting method did not require cold forming. Thus, omitting energy- and time-consuming production steps, the two novel manufacturing methods show both economic and ecological potential. Moreover, particle shaping showed the potential to reduce the sieving effort due to producing particles of equal size.

The tendency of metal effect pigment particles to form flow lines in weld lines was examined optically. Conventional platelet shaped pigment particles formed a characteristic flow line, in contrast to the absence of flow lines in case of tetrahedral pigment particles.

A 3D x-ray tomoscopy showed that the platelet shaped particles exhibit an orientation disturbance in the zone of the merging melt flows. In contrast, tetrahedral particles, which did not show a flow line in visible light, showed random orientation regardless of their position in the melt. By mapping the

particle production process and extending the process towards the manufacturability of other particle shapes.

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